

Chemical Structure and Upconversion Enhancement of NaYF₄ Nanocrystals and Nanosheets

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BSc (Hons)

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degree of Doctor of Philosophy

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Declaration of Authorship

I, Christian Clarke, declare that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also declare that the work presented is my own and the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis has been acknowledged. In addition, I declare that all information sources and literature used are indicated in the thesis.

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List of Acronyms

AFM	Atomic Force Microscopy
CCD	Charged Couple Device
CET	Cooperative Energy Transfer
CS	Core Shell
DFT	Density Functional Theory
EDS	Energy-dispersive X-ray Spectroscopy

EMU	Energy Migration Upconversion
ESA	Excited State Absorption
ETU	Energy Transfer Upconversion
FFT	Fast Fourier Transform
HTCP	High Temperature Co-Precipitation
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IMFP	Inelastic Mean Free Path
LSPR	Local Surface Plasmon Resonance
ML	Monolayer
NaYF ₄	Sodium Yttrium Fluoride
NEXAFS	Near Edge X-ray Adsorption Fine Structure
NIR	Near-infrared
OA	Oleic Acid
ODE	1-Octadecene
OM	Oleylamine
PA	Photon Avalanche
PDOS	Partial Density of States
PEY	Partial Electron Yield
PL	Photoluminescence
PMMA	Poly(methyl methacrylate)
RE	Rare Earth
SCCM	Standard Cubic Centimetre per Minute
SEM	Scanning Electron Microscopy
SLTD	Solid-Liquid-Thermal-Decomposition
SPAD	Single Photon Avalanche Diode
TCD	Thermal Co-Decomposition

TEA	Triethylamine
TEM	Transmission Electron Microscopy
TEY	Total Electron Yield
TFY	Total Fluorescent Yield
UCNP	Upconversion Nanoparticle
UV-Vis	Ultraviolet Visible
VASP	Vienna Ab initio Simulation Package
XRD	X-ray Powder Diffraction
XPS	X-ray Photoelectron Spectroscopy

List of Publications

Journal Publications

1. Xiaoxue Xu, **Christian Clarke**, Chenshuo Ma, Gilberto Casillas, Minakshi Das, Ming Guan, Deming Liu, Li Wang, Anton Tadic, Yi Du, Cuong Ton-That, Dayong Jin. “*Depth-profiling of Yb³⁺ sensitizer ions in NaYF₄ upconversion nanoparticles*” 2017, *Nanoscale* 9 (23) 7719-7726. [1]
2. Jiajia Zhou, Shihui Wen, Jiayan Liao, **Christian Clarke**, Sherif Abdulkader Tawfik, Wei Ren, Chao Mi, Fan Wang, Dayong Jin. “*Activation of the surface dark-layer to enhance upconversion in a thermal field*” 2018, *Nature Photonics* 12 (3), 154. [2]
3. **Christian Clarke**, Deming Liu, Fan Wang, Yongtao Liu, Chaohao Chen, Cuong Ton-That, Xiaoxue Xu, Dayong Jin. “*Large-scale dewetting assembly of gold nanoparticles for plasmonic enhanced upconversion nanoparticles*” 2018, *Nanoscale* 10 (14), 6270-6276. [3]

4. Wei Ren, Gungun Lin, **Christian Clarke**, Jiajia Zhou, Dayong Jin. “*Optical Nanomaterials and Enabling Technologies for High-Security-Level Anticounterfeiting*” 2019, *Advanced Materials* 32(18), 1901430. [4]
5. Du Ziqing, Abhishek Gupta, **Christian Clarke**, Matt Cappadona, David Clases, Deming Liu, Zhuoqing Yang, Shawan Karan, William Price, Xiaoxue Xu. “*Porous upconversion nanostructures as bimodal biomedical imaging contrast agents*” 2020, *Journal of Physical Chemistry C*, 124, 22, 12168–12174. [5]
6. Noushin Nasiri, **Christian Clarke**. “*Nanostructured Chemiresistive Gas Sensors for Medical Applications*” 2019, *Sensors* 19.3: 462. [6]
7. Noushin Nasiri, **Christian Clarke**. “*Nanostructured Gas Sensors for Medical and Health Applications: Low to High Dimensional Materials*” 2019, *Biosensors* 9(1), 43. [7]

(1 - 5 are closely related to my PhD program)

Oral Presentations

Xiaoxue Xu, **Christian Clarke**, Chenshuo Ma, Gilberto Casillas, Minakshi Das, Ming Guan, Deming Liu, Li Wang, Anton Tadich, Yi Du, Cuong Ton-That, Dayong Jin. “Depth-profiling of Yb³⁺ sensitizer ions in NaYF₄ upconversion nanoparticles” ICONN 2018, Wollongong, February 2018.

Abstract

The ability of lanthanide ions to convert lower energy photons to higher energy photons through the process known as upconversion presents as an opportunity to overcome limitations in sensitivity, efficiency and selectivity present for a wide variety of applications such as bio-imaging, photovoltaics and anti-counterfeiting.

Sodium Yttrium Fluoride (NaYF_4) is an inorganic insulator with low phonon energy ($360 \text{ cm}^{-1} \approx 45 \text{ meV}$), wide band gap (8.5 eV) and high chemical stability. These properties make NaYF_4 an ideal optical host crystal for lanthanide dopants to produce upconversion nanoparticles (UCNPs). The shape, size and structure of UCNPs can be highly controlled allowing them to be tailored to the requirements of specific applications.

Key challenges of concentration quenching and low quantum yield still confront UCNPs before their potential can be fully realised. Accordingly, enhancing the efficiency of UCNPs and their brightness has been the focus of numerous studies. In this project these challenges facing UCNPs are addressed by material characterisation and optimisation based on a comprehensive understanding of the chemical and optical properties of the material.

Firstly, synchrotron-based XPS and NEXAFS along with EDS and ICP-MS characterisation techniques were employed on a range of UCNPs with sizes from 13 nm - 51 nm and different lanthanide (Ln^{3+}) concentrations of 20% - 60% to determine how lanthanides are distributed within each nanocrystal. This analysis reveals a radial gradient distribution of Yb^{3+} and Tb^{3+} exists from the core to the surface of the NaYF_4 UCNPs, regardless of their size or lanthanide dopant concentration. The active core structure of this distribution was then systematically correlated to the optical properties of UCNPs with different sizes revealing a trend of increased optical upconversion emission efficiency by smaller sized UCNPs.

Secondly, surface plasmon coupling was achieved between core-shell UCNPs and dewetted gold nanoparticles by precisely growing NaYF_4 shell coatings of varied thickness from 5 nm - 15 nm around the optically active core UCNPs. The local

surface plasmon of the gold nanoparticles could be controlled and coupled with the internal transitions of the Er^{3+} ions. Combining these inert shelled UCNPs and plasmonic gold nanoparticles produced a shell thickness dependent enhancement with five times enhanced upconversion emission from the core-shell UCNPs with a shell thickness of 10 nm.

Thirdly, bulk NaYF_4 microparticles were successfully exfoliated to make 2D NaYF_4 nanosheets. By using a simple soft exfoliation method without the need for intensive ultrasonication atomically flat optically active nanosheets down to a single monolayer were produced. Extensive characterisation of the nanosheets supported by DFT calculations reveals a phase change and 1 eV band gap reduction for this new 2D material compared to the bulk.

Finally, in an appendix to demonstrate a massive three orders of magnitude increase in emission from ultra-small Tm^{3+} doped UCNPs an anti-counterfeiting mark was designed and fabricated. This enhancement only occurs at high temperature as activated surface phonons become efficient energy pathways for energy migration. The temperature dependence of the enhancement allowed the anti-counterfeiting mark to be temperature responsive.